WASTE STREAMS FROM HEXACHLOROPHENE MANUFACTURING PROCESSES

Prepared by:

Shrikant V. Kulkarni and Joseph A. Kowalski Radian Corporation 3200 E. Chapel Hill Road/Nelson Highway Research Triangle Park, North Carolina 27709

Prepared for:

Dr. Judy Bellin U.S. Environmental Protection Agency Office of Solid Waste (WH-565B) Washington, D.C. 20460

TABLE OF CONTENTS

	•				Paye
1.0	INTRODUCTION		•	i.	. 1-1
2.0	SUMMARY		•		. 2-1
3.0	HEXACHLOROPHENE	PRODUCTION AND WASTE CHARACTERIZATION	•		. 3-1
4.0	REFERENCES				. 4-1

WASTE STREAMS FROM HEXACHLOROPHENE MANUFACTURING PROCESSES

1.0 INTRODUCTION

The Environmental Protection Agency (EPA) has proposed to amend the regulations for hazardous waste management under the Resource Conservation and Recovery Act (RCRA). These amendments will include hazardous wastes containing certain chlorinated dioxins, -dibenzofurans, and -phenols.

The regulation includes wastes from the production of certain chlorophenols and chlorophenoxy pesticides, as well as discarded unused formulations containing tri-, tetra-, or pentachlorophenol and their derivatives. This proposed regulation designates as hazardous certain wastes (including reactor residues, still bottoms, brines, spent filter aids, spent carbon from product purification, and sludges from wastewater treatment), but not including untreated wastewater or spent carbon from:

- FO20 The production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri-, tetra-, or pentachlorophenol, or of intermediates used to produce their derivatives. This listing does not include wastes from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol (except wastewater and spent carbon from hydrogen chloride purification).
- F021 The manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzenes under alkaline conditions. (Except wastewater and spent carbon from hydrogen chloride purification.)
- FO22 The production of materials on equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of materials listed under FO20 and FO21. (Except wastewater and spent carbon from hydrogen chloride purification.)

FO23 - Discarded unused formulations containing tri-, tetra-, or pentachlorophenol, or discarded unused formulations containing compounds derived from these chlorophenols.

The waste will include those from both current and past manufacturing processes. In addition, wastes to be considered will include any FO20-FO23 waste associated with Superfund activities as well as any contaminated soils.

The following acronyms and definitions are used in this document to describe dioxin and furan compounds:

PCDDs = all isomers of all chlorinated dibenzo-p-dioxins.

PCDFs = all isomers of all chlorinated dibenzofurans.

CDDs & CDFs = all isomers of the tetra-, penta-, and hexachloro-dibenzo-p-dioxins and dibenzofurans, respectively.

TCDDs & TCDFs = all isomers of the tetrachlorodibenzo-p-dioxins and -dibenzofurans, respectively.

TCDD & TCDF = the respective 2,3,7,8-isomers.

The Environmental Protection Agency estimates that U.S. industries generated about 57 million metric tons (wet) of toxic or otherwise hazardous wastes in 1980. Of that amount, about 34 million metric tons, or 60%, came from the chemical and allied products industry. The volume of such wastes will grow about 3.5% annually, exceeding 80 million metric tons by 1990. EPA attributes much of the expected increase to sludges generated by air and water pollution control equipment and processes.

The production processes for chlorophenols and chlorophenol-based pesticides, such as the phenoxy herbicides, constitute the major sources of hazardous wastes containing chlorophenols, dioxins, and benzofurans (EPA, 1980). An extensive literature search has indicated that there is very limited information available on the specific product processes, the waste streams generated in these processes, and the characterization of these waste streams. This is particularly evident in the case of processes involving the manufacture of 2,4,5-trichlorophenol and products based on 2,4,5-trichlorophenol. The sensitivity of the issue involving the possible cogeneration of dioxins has made industry extremely reluctant

to impart any specific product process information. It is very often necessary, as it was in this instance, to extrapolate information obtained from various sources in order to prepare a waste generation and waste characterization profile for the hexachlorophene product process. Most of the information presented in this report is based on industrial contacts, process information available from similar operations as reported in various EPA pesticide reports, U.S. patents, and hands-on experience with actual industrial practices.

The objective of this report is to evaluate the production processes involved in the manufacture of hexachlorophene and the potential for cogeneration of dioxins. All waste streams and waste characteristics in this report are based on extrapolated information.

Table 2-1. WASTE STREAMS FROM HEXACHLOROPHENE MANUFACTURING PROCESSES

					Estimated Composition of Wastes			
Product	Waste Stream ID	-Waste Stream Description Waste Type		Estimated Waste Volume Per 1000 kg Product	% 2,4,5 TCP -	% Hexachlorophene	TCDD in ppb	
<u> </u>	X	Filter solids	Filtrol with adsorbed solvent	90-*110 kg	1-3	5-7	0.56 -0.90	
PESTICIDE GRADE HEXACHLOROPHENE	Y	Still bottoms - distillation residue	Non-volatile organic residue	500- 600 kg	3-4	0.5-0.9	1.50 -1.60	
	Z	Combined wastewaters	Aqueous	6000-9000 kg	0.03-0.05	0-0.001	0.007-0.012	
	A	Filter solids	Alkali-insoluble solids with adsorbed liquid	100- 160 kg	, 0-0.5	₹0.01	0.96 -1.20	
HARMACEUTICAL RADE EXACHLOROPHENE	В	Still bottoms - organic residues from crystallization	Solid/slurry	1030-1180 kg	24-25	48-50	1.40-1.50	
	C	Combined wastewaters	Aqueous	34000-37000 kg	0.05-0.08	0-0.003	0 -0.003	

^aSee process flow diagrams in Figures 3-1 and 3-2 for waste stream designations.

NOTE: Some of the quantities presented in the table have been rounded off.

3.0 HEXACHLOROPHENE PRODUCTION AND WASTE CHARACTERIZATION

Very little process-specific information is available concerning the manufacture of hexachlorophene. The production information presented in this chapter was obtained from U.S. patents 2,812,365 and 2,435,593. The process in U.S. patent No. 3,607,949 involving the use of 2,4,5-trichlorophenylsulfate was not considered viable on an industrial scale.

The process discussed in U.S. patent 2,812,365 (November 5, 1957; assigned to Givaudan Corporation) involves the use of sulfuric acid as a condensing agent in a halogenated solvent such as ethylene dichloride. The procedure does not indicate any further purification of the product. The lack of information and the use of the chlorinated hydrocarbon solvent in its manufacture prompts us to classify the product as pesticide grade hexachlorophene.

The process discussed in the U.S. patent 2,435,593 (February 10, 1948; assigned to Burton T. Bush, Inc., New York) involves condensation of 2,4,5-trichlorophenol in the presence of sulfuric acid followed by an elaborate procedure to remove non-phenolic water-insoluble impurities. The final step is crystallization of a pure product. This process, it is believed, will lead to pharmaceutical grade hexachlorophene, the use of which is regulated by the Food and Drug Administration (FDA) because of its potential neurotoxicity in humans (The Merck Index, 1976).

3.1 MANUFACTURE OF HEXACHLOROPHENE

Industry information indicates that Givaudan Corporation is the only current manufacturer of hexachlorophene in the United States (B. Turetsky, Givaudan Corporation, personal communication, 1984). Since most of the dioxins are cogenerated in the dechlorination reaction during the manufacture of 2,4,5-trichlorophenol, it is desirable to

employ only highly purified 2,4,5-trichlorophenol for the manufacture of hexachlorophene in order to minimize the dioxin content in the final product. The starting 2,4,5-TCP material used to produce hexachlorophene was assumed to have 1 part per billion (ppb) of 2,3,7,8-TCDD as a raw material specification (personal communication).

Since the suspension and cancellation of the major uses for 2,4,5-trichlorophenoxyacetic acid, Silvex, and other 2,4,5-TCP-based pesticides in 1979, the manufacture of 2,4,5-TCP appears to have been terminated in the United States. Up until the suspension of the uses, the voluntary limit on the TCDD content for 2,4,5-T by the manufacturers was considered to be 100 ppb. However, it should be technically feasible to manufacture 2,4,5-TCP with less than 100 ppb TCDD based on raw material specifications required for hexachlorophene production. Currently, 2,4,5-TCP is supplied to Givaudan Corporation by Chemie Linz Aktiengesellschaft of Linz, Austria. The TCDD content in the Chemie Linz 2,4,5-TCP is unknown.

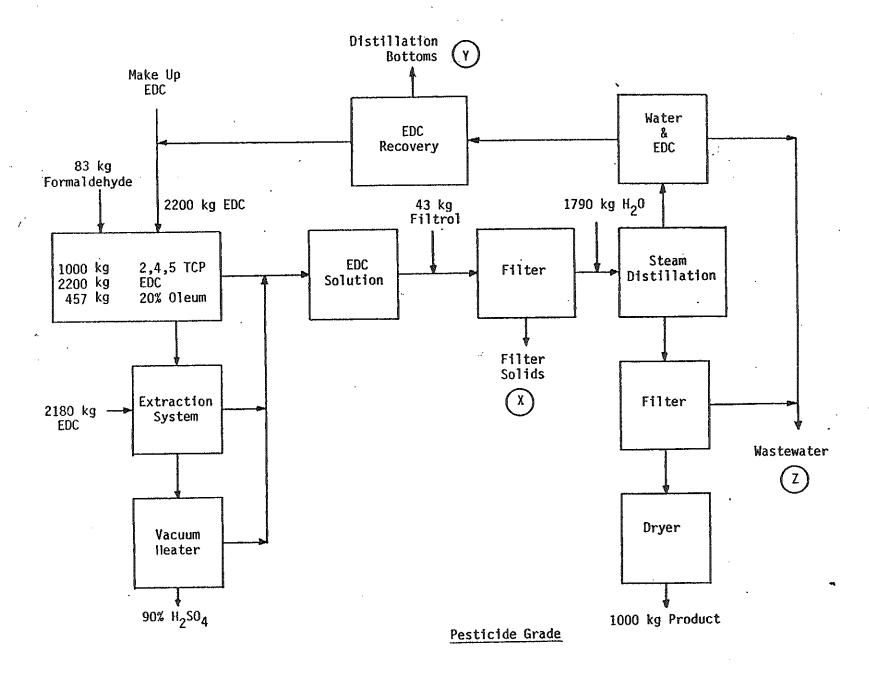
3.2 PROCEDURE FOR ENGINEERING ESTIMATES

Development of an engineering estimate of waste products formed by the hexachlorophene manufacturing process followed the following procedure:

- (1) Amounts used in the reactions were calculated by chemical stoichiometry.
- (2) The actual amounts used in the processes were obtained from cited U.S. patents.
- (3) Differences between actual amounts and stoichiometric amounts were considered waste losses from the system. The losses were distributed among the various waste streams depending upon the unit operation generating the waste stream.
- (4) Additional waste products formed by known chemical transformations were estimated.

3.3 MANUFACTURE OF PESTICIDE GRADE HEXACHLOROPHENE

U.S. patent 2,812,365 was used in extrapolating information to develop the process flow diagram (Figure 3-1) and the waste stream characteristics for what is considered pesticide grade hexachlorophene.



Pesticide Grade

Figure 3-1. Bis(3,5,6-Trichloro-2-Hydroxyphenyl) Methane Process Flow Diagram. Source: U.S. Patent 2,812,365

The hexachlorophene is prepared by the condensation of two moles of 2,4,5-trichlorophenol with one mole of formaldehyde in the presence of concentrated sulfuric acid and ethylene dichloride.

$$2 + CH_2O \xrightarrow{H_2SO_4} CH_2 \xrightarrow{OH} CH_2 + H_2O$$

3.3.1 Chemical Stoichiometry

The stoichiometry of the chemical reactions in pesticide grade hexachlorophene production are presented below. All equations are based on a final product volume of 1000 kilograms.

(1) Two moles 2,4,5-TCP/mole product

$$\frac{2(198) \times 1000 \text{ kg}}{407} = 973 \text{ kg/}1000 \text{ kg hexachlorophene product}$$

(2) One mole Formaldehyde/mole product

$$\frac{30x\ 1000\ \text{kg}}{407} = 73.7\ \text{kg/1000}\ \text{kg hexachlorophene product}$$

- (3) The chemical reactions required to form hexachlorophene occur more rapidly in the presence of certain halogenated hydrocarbon solvents, such as ethylene dichloride (EDC). The amount of EDC specified by the patent is equivalent to 6580 kg per 1000 kg of hexachlorophene product.
- (4) Water is formed during the coupling reaction between 2,4,5-TCP and formaldehyde.

$$\frac{18 \times 1000 \text{ kg}}{407} = 44.2 \text{ kg/}1000 \text{ kg hexachlorophene product}$$

3.3.2 Losses

The stoichiometric equations provide the actual amount of starting material required to produce 1000 kg of product. The starting material quantities, obtained from the patent, minus the stoichiometric quantities as developed in Section 3.1.1, equal the waste losses of the process. The process losses are characterized according to starting materials and known chemical transformation products. The losses are summarized in Table 3-1.

The material lost is considered to be distributed among the various waste streams. The distribution is estimated and based on factors such as efficiency of the unit operation, properties of the starting materials, and waste properties. For example, solvent recovery in a unit batch operation is assumed to be 90%, with the remaining 10% being a waste product. In practice, 90% recovery is rarely obtained. The estimated distribution of the waste constituents among the various waste streams from the manufacture of pesticide grade hexachlorophene are shown below.

(1) 2,4,5-TCP

1000 kg - 973 kg = 27 kg

Actual distribution of the 27 kg of 2,4,5-TCP among the identified waste streams may be:

- a. In EDC solution adhered to filtrol approximately 3-10% (1-3 kg)
- b. Solvent recovery still bottoms approximately 80% of 2,4,5-TCP (20 kg)
- c. Water streams approximately 5-15% of 2,4,5-TCP (2-4 kg)
- d. Final product approximately 1% of 2,4,5-TCP (0.3 kg)

(2) Formaldehyde

$$83 \text{ kg} - 73.7 \text{ kg} = 9.3 \text{ kg}$$

a. Most of the remaining formaldehyde will be lost in the aqueous phase. Some transformation may also occur, producing unwanted byproducts such as s-trioxane and formic acid (Fuson, 1964)

Table 3-1. TO OBTAIN 1000 KILOGRAMS FINAL PRODUCT

Starting Material	Starting Quantity (kg)	Material Used (kg)	* Waste Loss (kg)
2,4,5-TCP	1000	973	27
Formaldehyde	83	73.7	9.3
Ethylene dichloride	6580		0-600
Filtrol	43		43

(3) Ethylene dichloride

It is assumed that up to 10% of the total EDC used in the process is lost (0-600 kg). The remaining 90% is recovered for reuse. The losses are assumed to be distributed among the following waste streams:

- a. To atmosphere during handling approximately 5-10% (40-50 kg)
- Solvent recovery still bottoms approximately 80-90% (500-550 kg)
- c. Steam distillation approximately 10% (50-60 kg)
- d. Filter solids approximately 5-10% (40-50 kg)
- (4) Filtrol used as filter aid is a solid waste (43 kg).
- (5) The total wastewater stream is approximately 1 gallon per kilogram of final product (U.S. Patent 2,812,365).
- (6) An assumption was made that the sulfuric acid would not be recovered. Considering the amounts of sulfuric acid involved, it may be cost effective to neutralize and dispose of the sulfate in an aqueous waste stream. If this is the case, sodium hydroxide must be added to the acid stream to neutralize it.

$$\frac{548 \text{ kg H}_2\text{SO}_4}{98} = 5.6 \text{ moles H}_2\text{SO}_4$$

$$H_2SO_4 + 2 NaOH \longrightarrow Na_2SO_4 + 2 H_2O$$

- 5.6 moles \times 2 = 11.2 moles NaOH
- 11.2 moles \times 40 = 448 kg NaOH/1000 kg hexachlorophene product
- (7) TCDD in waste streams The starting 2,4,5-TCP material was assumed to contain 1 ppb of dioxins. The expected distribution of the dioxins from 1000 kg of 2,4,5-TCP (required to manufacture 1000 kg of hexachlorophene) in the three waste streams

is shown below. It was assumed that no dioxins were formed during the manufacture of the pesticide grade hexachlorophene.

- a. Filter solids approximately 5-10% (50-100 x 10^{-9} kg)
- b. Still bottoms approximately 80-90% ($800-900 \times 10^{-9}$ kg)
- c. Wastewaters approximately 5-10% (50-100 x 10⁻⁹ kg)

The pesticide grade hexachlorophene waste stream characteristics are shown in Table 3-2. The quantities of the waste constituents are given in kg/1000 kg of final product. The percent composition is determined by taking the constituent waste quantity, dividing by the total waste stream quantity, and multiplying by 100.

3.4 MANUFACTURE OF PHARMACEUTICAL GRADE HEXACHLOROPHENE

U.S. Patent 2,435,593 was used to develop the process flow diagram (Figure 3-2) and the waste stream characteristics for the production of pharmaceutical grade hexachlorophene.

The pharmaceutical grade hexachlorophene is prepared by reacting two moles of 2,4,5-trichlorophenol and a suitable formaldehyde-yielding material at an elevated temperature in the presence of a minor amount of strong sulfuric acid for thirty minutes. The unique part of the pharmaceutical grade process is the purification method, which involves convertion of hexachlorophene to its sodium salt in solution, extraction of the non-phenolic organics, and reprecipitation of the product prior to its crystallization.

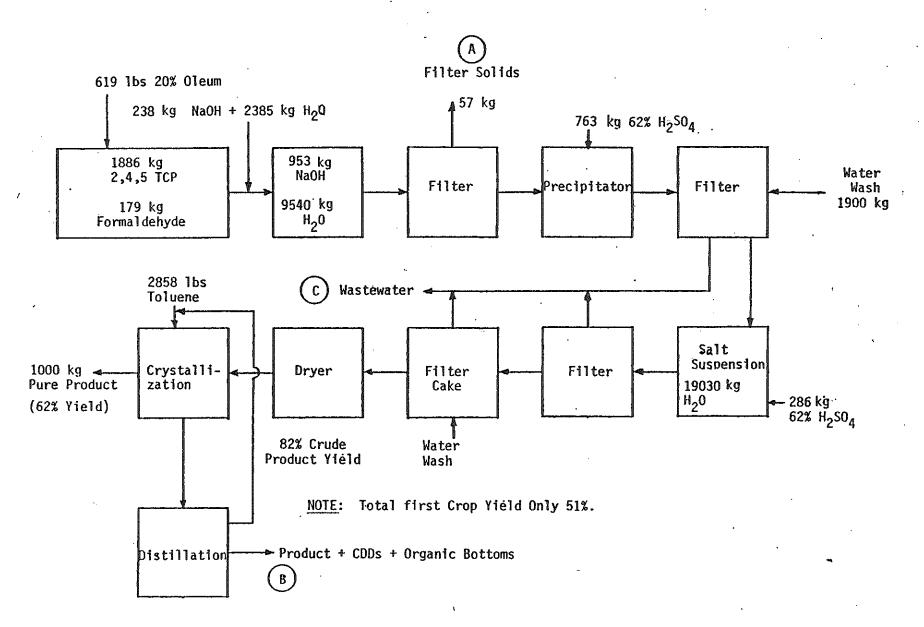
$$2 \xrightarrow{CI} \xrightarrow{CH_2O} \xrightarrow{CH_2O} \xrightarrow{CI} \xrightarrow{CH_2 OH} \xrightarrow{CI} \xrightarrow{N_2OH} \xrightarrow{CI} \xrightarrow{N_2OH}$$

Table 3-2. PESTICIDE GRADE HEXACHLOROPHENE WASTE STREAM CHARACTERIZATION

Filter (Waste S		Solids tream X)	Still Bottoms (Waste Stream Y)		Combined Wastewaters (Waste Stream Z)	
Waste Constituent	Quantity (kg/1000 kg Product)	Percent Composition	Quantity (kg/1000 kg Product)	Percent Composition	Quantity (kg/1000 kg Product)	Percent Composition
Filtrol	40-43	38-45			 . ·	
2,4,5-TCP	1-3	1-3	18-20	3-4	2-4	0.03-0.05
Hexachlorophene	5-8	5-7	3-5	0.5-0.9	<0.1	<0.001
Formaldehyde	₹1.0	<1.0	<1.0	<0.1	<2	<0.03
S-Trioxane	<0.1	<0.1	<0.1	<0.02	<2.4	<0.03
EDC & Non-volatile Organic Residue			500-550	94-95		
Formic Acid			<1.0	<0.1	<2	₹0.03
Na ₂ SO ₄				*******	800-850	9-12
EDC EDC	40-50	44-45			50-60	0.6-0.7
Water	1-5	1-5	<1.0	<0.1	6000-8000	87-90
2,3,7,8-TCDD	50-100 ×10-9	56-90 ×10 ⁻⁹	800-900 ×10 ⁻⁹	152-156 ₋₉	50-100 ₋₉ ×10	0.70-1.12 ₋₉ ×10
Total	89-111	<u>,</u>	525-579		6862-8924	

Example calculation of % TCDD: $\frac{50 \times 10^{-9} \text{ kg}}{1000 \text{ kg product}} \div \frac{89 \text{ kg}}{1000 \text{ kg product}} \times 100 = \frac{56 \times 10^{-9} \%}{100} = 0.56 \text{ ppt}$

NOTE: See process flow diagram (Figure 3-1) for location of waste streams.



Pharmaceutical Grade

Figure 3-2. Bis(3,5,6-Trichloro-2-Hydroxyphenyl) Methane Process Flow Diagram Source: U.S. Patent 2,435,593

3.4.1 Chemical Stoichiometry

The chemical stoichiometry associated with the production of pharmaceutical grade hexachlorophene is presented below. All equations are based on obtaining 1600 kg of crude product before crystallization (U.S. Patent 2,435,593). The actual first crop yield after crystallization (final product) is 1000 kg.

- (1) Two moles 2,4,5-TCP used/mole crude product $\frac{2(198) \times 1600 \text{ kg}}{407} = 1557 \text{ kg } 2,4,5\text{-TCP used/}1600 \text{ kg crude product}$
- (2) One mole formaldehyde used/mole product $\frac{30 \times 1600 \text{ kg}}{407} = 118 \text{ kg formaldehyde used/1600 kg crude product}$
- (3) One mole sodium hydroxide/mole product $\frac{40 \times 1600 \text{ kg}_{157.2} \text{ kg caustic/1600 kg crude product}}{407}$
- (4) Two moles NaOH are required to neutralize one mole H_2SO_4 $2NaOH + H_2SO_4 \longrightarrow NaSO_4 + 2 H_2O$ $Total\ acid = 0.62\ (1049\ kg) + 619 = 1269\ kg$ $\frac{1269}{98} = 12.9\ moles\ H_2SO_4$ $2(12.9)\ moles\ NaOH\ x\ 40 = 1035\ kg\ NaOH$
- (5) Water formed during coupling of 2,4,5-TCP and paraformaldehyde $\frac{18 \times 1600 \text{ kg}}{407} = 70.8 \text{ kg water/}1600 \text{ kg crude product}$

3.4.2 Losses

The waste streams are characterized according to starting materials and known chemical transformation products. Losses are summarized in Table 3-3.

Table 3-3. TO OBTAIN 1600 KILOGRAMS CRUDE PRODUCT

Starting Material	Starting Quantity (kg)	Material Used (kg)	/ Waste Loss (kg)
2,4,5-TCP	1886	1557	329
Formaldehyde	179	118	61

(1) 2,4,5-TCP

1886 kg - 1557 kg = 329 kg

Assumed distribution of the 329 kg of 2,4,5-TCP among the identified waste streams may be:

- a. Water streams approximately <1% (<0.5 kg)
- b. Final product approximately 75-90% (250-300 kg)
- Solvent recovery still bottoms approximately 6-9% (20-30 kg)

(2) Formaldehyde

179 kg - 118 kg = 61 kg

- a. Most of the remaining formaldehyde is lost in the aqueous phase. Some transformations are likely to occur to form such byproducts as s-trioxane and formic acid (Fuson, 1964).
- (3) The pharmaceutical grade process produces approximately four times as much wastewater as the pesticide process (U.S. Patent 2,435,593). The total wastewater stream is approximately 4 gallons per kilogram of final product.
- (4) TCDDs in waste streams The starting 2,3,5-TCP material was assumed to contain 1 ppb of TCDD. The total TCDDs associated with 1886 kg of 2,4,5-TCP will be distributed among the three waste streams shown below. Formation of dioxins on the alkali salt and subsequent coupling of sodium 2,4,5-trichlorophenate may increase the TCDD concentration in the three waste streams, but it will not be considered here.
 - a. Filter solids approximately 5-10% (100-200 \times 10⁻⁹ kg)
 - b. Still bottoms approximately 80-90% (1500-1700 \times 10⁻⁹ kg)
 - c. Wastewaters approximately <5% (<100 x 10⁹ kg)

The pharmaceutical grade hexachlorophene waste stream characteristics are summarized in Table 3-4. The quantities of the waste constituents are given in kg/1000 kg of final product. The percent composition is calculated as shown in the example at the bottom of the table.

Table 3-4. PHARMACEUTICAL GRADE HEXACHLOROPHENE WASTE STREAM CHARACTERIZATION

	Filter Solids (Waste Stream A)		Still Bottoms (Waste Stream B)		Combined Wastewaters (Waste Stream C)	
Waste Constituent	Quantity (kg/1000 kg Product)	Percent Composition	Quantity (kg/1000 kg Product)	Percent Composition	Quantity (kg/1000 kg Product)	Percent Composition
Na ₂ SO ₄	1-3	0.96-1.80			1800-1850	5.0-5.4
Formaldehyde	<1.0	<1.0	<1.0	<0.1	<35	0.09-0.10
S-Trioxane	<0.3	<1.0	<0.2	<0.01	₹3.0	0.008-0.009
Formic Acid	<1.0	<1.0	<1.0	<0.1	<15	0.04-0.043
Hexachlorophene		-	· ·		<1.0	0.002-0.003
Crude Hexachlorophene and Isomers			500-600	48-50	· 	
Toluene & Nonvolatile Organic Residue		•	285	23-27		
Alkali-Insoluble Material	50-60	36-48	, 		****	
2,4,5-TCP	<0.5	<1.0	250-300	24-25	20-30	0.05-0.08
Water	50-100	48-60		<u></u>	33000-35000	9 4-95
2,3,7,8-TCDD	100-200 x 10 ⁻⁹	96-120 ×10-9	1500-1700 ₋₉	140-145 ₋₉	<100x10 ⁻⁹	<0.28×10 ⁻⁹
Total	104-166		1038-1188		34874-36934	

NOTE: See process flow diagram (Figure 3-2) for location of waste streams.

3.5 WASTE STREAM CHARACTERISTICS

Three waste streams were identified in the production of each grade of hexachlorophene (see Figure 3-1 and 3-2). The assumed characteristics of each waste stream are based on the chemical starting materials, the known possible chemical transformations, and the manufacturing unit operations. The stream constituents and concentrations are summarized in Tables 3-2 and 3-4.

3.5.1 Waste Stream X and A (Filter Solids)

Based on a TCDD contaminant level of 1 ppb in the starting 2,4,5-TCP, it was estimated that TCDDs concentration in the filter solids from the manufacture of hexachlorophene would be in the range of $0.50-1.20~\rm ppb$.

3.5.2 Waste Stream Y and B (Still Bottoms)

The level of TCDDs found in the still bottoms in stream B and Y were estimated to be between 1 and 2 ppb. The possible formation of additional dioxin by the self condensation of sodium 2,4,5-trichlorophenate was not considered in estimating the TCDD levels.

$$c_{i} \xrightarrow{OH} c_{i} + c_{i} \xrightarrow{ON_{\alpha}} c_{i} \xrightarrow{ON_{\alpha}} c_{i} \xrightarrow{ON_{\alpha}} c_{i} \xrightarrow{ON_{\alpha}} c_{i} + N_{\alpha}C_{i}$$

In the pharmaceutical grade process, conditions are more favorable for the formation of TCDD in the distillation step. The availability of a sodium salt and potential high temperatures makes the formation of TCDD possible; however, the estimates are not available (Bovey & Young, 1980).

3.5.3 Waste Stream Z and C (Wastewaters)

The concentration of TCDDs in the wastewaters for either process was estimated to be low (<0.01~ppb) because TCDDs are very insoluble in water and are expected to be part of the organic waste streams (EPA, 1980).

3.6 CHLORINATED DIOXINS AND BENZOFURANS IN HEXACHLOROPHENE WASTES

As was earlier mentioned, the analytical characterization of the process wastes from the manufacture of hexachlorophene are not available. The engineering estimates for these waste streams are based on the initial assumption that the 2,3,7,8-tetrachlorodibenzodioxin (TCDD) concentration in the highly purified starting 2,4,5-trichlorophenol may be on the order of 1 part per billion.

According to the EPA proposed rule (40 CFR Parts 261, 264, 265, and 775; Federal Register 14513, April 4, 1983) for hazardous waste management systems, all CDDs and CDFs identified or proposed to be identified in Appendix VIII are considered as toxicants of concern. No data on the relative concentrations of tetra-, penta-, hexa-, hepta-, or octa-chlorodibenzodioxins (CDDs) and chlorodibenzofurans (CDFs) in starting materials are available. If the relative concentration of the specific chlorodibenzodioxin isomers (CDDs) and chlorodibenzofuran isomers (CDFs) were known for the starting 2,4,5-trichlorophenol, it would be possible to estimate the quantities of these isomers. Similarities between the properties of all CDDs and CDFs would make this possible.

3.7 RECOMMENDATION FOR FUTURE WORK

Because there is only one manufacturer of hexachlorophene in the United States, it is recommended that reliable waste generation and waste management information be obtained under Section 3001 of Resource Conservation and Recovery Act (RCRA) of 1976. This information would be used to substantiate the generic listing of F020 as a hazardous waste, including the exclusion of the wastes from the production of hexachlorophene using highly purified 2,4,5-trichlorophenol.

4.0 REFERENCES

- EPA (1980), "Dioxins: Volume 1 Sources, Exposure, Transport, and Control." EPA-600/2-80-156.
- 2. The Merck Index, Ninth Edition, 1976. Martha Windholz, ed. Merck and Co., Inc. Rahway, New Jersey.
- 3. Fuson, Reynold. Reactions of Organic Compounds. John Wiley and Sons (1964). pg. 393.
- 4. Bovey, R. and A. Young (1980). The Science of 2,4,5-T and Associated Phenoxy Herbicides. Wiley Interscience.
- 5. U.S. Patent 2,812,365. Process of Preparing Bis-(3,5,6-Trichloro-2-Hydroxyphenyl) Methane. Patented Nov. 5, 1957, United States Patent Office.
- 6. U.S. Patent 2,435,593. Process for Making Bis-(3,5,6-Trichloro-2-Hydroxyphenyl) Methane. Patented Feb. 10, 1948, United States Patent Office.
- 7. U.S. Patent 3,607,949. Production of 2,2'-Methylenebis (3,4,6-Trichlorophenol). Patented Sept. 21, 1971, United States Patent Office.



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OFFICE OF SOLID WASTE AND EVERYOUND ENDED WASTE AND EVERYOUND ENDED WISE RE: WIBFSJ0240

Mr. John Angiolini Givaudan Corporation 125 Delawanna Avenue Clifton, NJ 07014

Dear Mr. Angiolini,

Pursuant to our telephone conversation of April 9, I am enclosing the engineering analysis of the Hexachlorophene (HCP) manufacturing process performed for us by Radian Corporation. We would appreciate your review of this document. In particular, we would like you to verify its accuracy as it applies to your manufacturing process.

In addition, we request your comments on the following:

- 1. What are the specifications of the 2,4,5-TCP used for the manufacture of pharmaceutical and pesticide grade HCP?
- 2. Please provide us with analytical data presently available to you for concentrations of dibenzofurans, and, tetra-, penta-, and hexachlorodioxins, including 2,3,7,8-TCDD in a) 2,4,5-TCP feedstock; b) HCP products, and c) the waste streams. If no analytical data is available please exercise your best judgement in estimating the levels of concentration (to the ppb level).
- 3. Please tell us whether you re-crystallize after the first crystallization product, and whether the mother liquid is discarded or re-used, and, if the latter, how often it is recycled.
- 4. Did Radian Corporation correctly identify the process flow and waste streams? If not, please correct.
- 5. Is wastewater from the HCP process independently disposed, or is it co-mingled with wastewater from other processes? How is it disposed (e.g., settling pond, discharged (where?)) with or without treatment? If the latter, what treatment?

If you have any questions, please call our contractor, Dr. Shri Kulkarni at Radian Corporation (919-541-9100). Thank you in advance for your cooperation. We look forward to your early reply.

Sincerely,

Francine S. Jacoff Program Manger Listing Program

Enclosure